

45 6,521,694

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁷ : C08F 8/04, C08C 19/02</p>	<p>A1</p>	<p>(11) International Publication Number: WO 00/09576 (43) International Publication Date: 24 February 2000 (24.02.00)</p>
<p>(21) International Application Number: PCT/NL99/00507 (22) International Filing Date: 9 August 1999 (09.08.99) (30) Priority Data: 1009841 11 August 1998 (11.08.98) NL (71) Applicant (for all designated States except US): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): BELT, Johannus, Wilhelmus [NL/NL]; Spaans Neerbeek 23, NL-6164 CH Geleen (NL). VERMEULEN, Jacobus, Adriaan, Antonius [NL/NL]; Skimmiastraat 21, NL-6163 MH Geleen (NL). KÖSTERMANN, Mike [DE/NL]; Wezelstraat 27, NL-5854 JA Nieuw-Bergen (NL). (74) Agent: DORRESTIJN, Antoon; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).</p>		<p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report.</p>
<p>(54) Title: PROCESS FOR HYDROGENATION OF CARBON-CARBON DOUBLE BONDS OF AN UNSATURATED POLYMER</p>		
<p>(57) Abstract</p> <p>The invention relates to a process for hydrogenating carbon-carbon double bonds of an unsaturated polymer by adding to the unsaturated polymer (1) a reducing agent selected from the group comprising hydrazines and hydrazine-releasing compounds, (2) an oxidising compound and (3) a catalyst, wherein the catalyst contains an element from group 13 of the Periodic Table of the Elements.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LJ	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

5 PROCESS FOR HYDROGENATION OF CARBON-CARBON DOUBLE BONDS
 OF AN UNSATURATED POLYMER

 The invention relates to a process for
hydrogenating carbon-carbon double bonds of an
10 unsaturated polymer by adding to the unsaturated
polymer (1) a reducing agent selected from the group
comprising hydrazines and hydrazine-releasing
compounds, (2) an oxidising compound and (3) a
catalyst.

15 A similar process is known from US
4,452,950. This patent discloses that the reduction of
carbon-carbon double bonds of an unsaturated polymer,
with the polymer having been brought into the latex
form, is carried out in the presence of a metal ion
20 initiator. The metal ion initiator is a metal compound
that reacts with hydrazine and is reduced by the
hydrazine to a lower valence state. Examples of
suitable metal ion initiators are Cu and Fe sulphates.
After all reactants are added, the mixture is heated to
25 the reflux temperature of the reaction mixture.

 A drawback of this process is that the
polymer is crosslinked early in the hydrogenation
process and that heavy metals are left behind in the
polymer after it is worked up.

30 The present invention aims to eliminate
these drawbacks.

 To that end, the invention provides a

process in which the catalyst contains an element from group 13 of the Periodic Table of the Elements.

The Periodic Table of the Elements as used in the present application is published on the inside
5 of the cover of the Handbook of Chemistry and Physics, 67th edition, 1986-1987 in accordance with the latest IUPAC nomenclature.

Furthermore, the process of the present invention presents the advantage that the reducing
10 agent and oxidising compound may be present in equimolar amounts to at the most a minor excess relative to the double bonds of the unsaturated polymer to be reduced.

Also, the reaction is catalysed so well
15 that a heating step may be omitted so that the hydrogenation process is much simplified.

Crosslinking of the latex during the hydrogenation process as described in US 4,452,950 is mentioned in US 5,039,737 and US 5,442,009. Both
20 Patents disclose a process for breaking up the gel structures through post-treatment with ozone.

From application WO 91-A-06579 it is known to carry out a hydrogenation in the absence of a catalyst. However, this process employs a high
25 hydrazine-to-unsaturated-polymer molar ratio in order to obtain a non-crosslinked polymer. Excess hydrazine subsequently needs to be worked up and destroyed, which from an economics point of view is costly and from an environmental point of view is unacceptable.

30 The unsaturated polymers that can be hydrogenated via the process of the present invention

are composed of 5-100% by weight of a conjugated diene-monomer unit and 95-0% by weight of a vinyl-unsaturated monomer unit. Specific examples of conjugated diene-monomer units are 1,3-butadiene, 2,3-dimethyl
5 butadiene, isoprene and 1,3-pentadiene. Specific examples of vinyl-unsaturated monomer units are nitriles (for example acrylonitrile and methacrylonitrile), vinyl aromatic hydrocarbons (for example styrene, (o-, m-, p-) alkylstyrenes and
10 divinylbenzene) dialkenyl aromatics (for example diisopropenyl benzene), unsaturated carboxylic acids and esters thereof (for example acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid, methyl acrylate, ethyl acrylate, butyl acrylate,
15 2-ethylhexyl acrylate and methyl methacrylate), vinylpyridine and vinyl esters (for example vinyl acetate).

The unsaturated polymers may be prepared in different manners for example through emulsion
20 polymerisation, solution polymerisation and bulk polymerisation.

Specific examples of suitable unsaturated polymers are polybutadiene, polyisoprene, styrene-butadiene copolymers (SBR), acrylonitrile-butadiene
25 copolymers (NBR), natural rubber, butadiene-isoprene rubber and terpolymers of butadiene, acrylonitrile and butylacrylate or acrylic acid.

Most preferably NBR is used.

The unsaturated polymers hydrogenated via
30 the process of the present invention are characterised in that their backbone chain contains carbon-carbon

double bonds that have an adverse effect on the polymer's thermal, photochemical and oxidative stability.

During the hydrogenation, the unsaturated
5 polymers preferably are present in the latex form. The latex form is an aqueous emulsion of polymer, in which sundry additives for example soap and stabilisers may be present. A description of the latex form which is suitable for the hydrogenation of unsaturated polymers
10 via the process of the invention is given in for example US 5,442,009.

The latex of the unsaturated polymer may be hydrogenated as such. The polymer concentration in the latex is in the range of from 1 to 70% by weight,
15 preferably between 5 and 40 %wt.

The reducing agent is selected from the group comprising hydrazines and hydrazine-releasing compounds for example hydrazine hydrates, hydrazine acetate, hydrazine sulphate and hydrazine
20 hydrochloride. If the unsaturated polymer is hydrogenated in latex, use is preferably made of hydrazine and hydrazine hydrate. Alternative hydrazine sources may be used if hydrogenation is effected in solution or in the melt and if the alternative
25 hydrazine sources do not adversely effect the stability of the latex.

Latices formed from, for example, non-ionic soaps may be used in combination with hydrazine, hydrazine hydrate, hydrazine hydrochloride and
30 hydrazine sulphate.

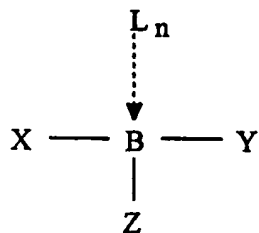
The hydrazine or hydrazine releasing

compound preferably is present in a molar ratio of from 0.1:1 to 100:1 relative to these carbon-carbon double bonds. Preferably, this ratio lies between 0.8:1 and 5:1, most preferably between 0.9:1 and 2:1.

5 Oxidising compounds that are suitable for the process of the invention are for example air, oxygen, ozone, peroxides, hydroperoxides, iodine, iodates, hypochlorite and similar compounds. Particularly suitable oxidising compounds are selected
10 from the group consisting of peroxides and hydroperoxides. Most preferably, use is made of hydrogen peroxide.

The oxidising compound is preferably present at a molar ratio of 0.1:1 to 100:1 relative to
15 the carbon-carbon double bonds. More preferably, this ratio is between 0.8:1 and 5:1, most preferably between 0.9:1 and 2:1.

It is preferred for the catalyst be a compound which contains boron (B). Examples of
20 preferred B-containing catalysts are compounds of the general formula



25 where X, Y and Z are chosen independently of one another from the group comprising R, =O, OR, OOR, NR₂, SR, PR₂, OC(=O)R and halogen atoms, where R is a H atom

or an alkyl, aryl or cycloalkyl group having 1-20 carbon atoms, or a hydrocarbon group having 1-20 C atoms and containing a heteroatom from groups 14, 15, 16 and 17 of the Periodic Table of the Elements, or a polymerchain containing one or more polar groups; wherein X and Z and optionally Y may form a bridge; L is an electron-donating ligand, which may be bonded to either X, Y or Z; n = 0, 1 or 2.

Examples of suitable electron-donating ligands are for example water, an alcohol, pyridine, bipyridine, triazine, pyrrole compound, an imidazole compound, a pyrazole compound, a pyrimidine compound and a pyrazine compound, an ester, ether, a furan, tetrahydrofuran, pyrans, dioxan, phosphine, phosphide, phosphate, a thio compound or a polymer, for example a polyvinylalcohol or polyethyleneoxide.

Salts of abovementioned boron-containing compounds might also be applied.

Preferably L is chosen from the group comprising diols, polyvinylalcohols and polyethyleneoxide.

It is preferred for the catalyst to be chosen from the group consisting of borates, peroxiborates and boric acid (H_3BO_3). More preferably, the catalyst is boric acid. It is most preferred that boric acid is used in combination with a polyvinylalcohol.

The catalyst of the present invention may be combined with the oxidising compound so that less or no oxidising compound needs to be added separately. An example of a catalyst that also has an oxidising effect

is peroxiborate.

Another preferred embodiment of the present invention is addition of boric acid to the reaction mixture together with the peroxide or hydroperoxide.

5 The molar ratio of the catalyst to the carbon-carbon double bonds of the unsaturated polymer is between 1:1000 and 10:1. The ratio preferably is between 1:50 and 1:2.

 The order in which the compounds are added
10 for the hydrogenation reaction may in principle be random. Preferably, however, the oxidising compound is added last and in such a way that the concentration of the oxidising compound remains low during the hydrogenation reaction.

15 The degree of hydrogenation is the percentage of carbon-carbon double bonds that is saturated after the hydrogenation reaction relative to the initial amount of double bonds. The process of the present invention provides polymers that as a rule
20 have a degree of hydrogenation higher than 60%. Preferably, the degree of hydrogenation is higher than 80%. The process is eminently suitable for preparing polymers having a degree of hydrogenation higher than 90%.

25 The hydrogenation reaction temperature normally is between 0° and 250°C. The temperature preferably is between 20° and 100°C. A reaction temperature between 40° and 80°C is particularly preferable. Most preferable is a reaction temperature
30 between 60 °C and 80 °C, which results in a high catalyst activity, so that low catalyst concentrations

can be used.

During hydrogenation in a latex, a minor amount of solvent for the unsaturated polymer may be present. In that case, the amount of solvent may vary
5 between 0 and 20%wt (solvent relative to polymer).

The hydrogenation time normally is between 30 minute and 24 hours. The hydrogenation time preferably is between 1 hour and 12 hours.

The process is illustrated by the following
10 examples without being limited thereto.

In almost all cases the degree of hydrogenation was determined with the aid of $^1\text{H-NMR}$ in a Bruker 200 MHz instrument. The measurement was conducted on polymer precipitated in isopropanol, that
15 was after precipitation dried with filter paper and immediately dissolved in deuterated chloroform. The degree of hydrogenation was calculated from the ratio of the integrals of the olefinic protons, which are between 5.2 and 5.6 ppm, and the proton adjacent to the
20 nitrile group, being between 2.35 and 2.65 ppm.

In some cases (expressly indicated) the degree of hydrogenation was determined by Raman spectroscopy (using a Spectrum 2000 NIR FT Raman instrument).

25 The C=C stretch vibrations of the vinyl, cis and trans bonds can be seen in the Raman spectrum between 1600 and 1700 cm^{-1} . The C \equiv N stretch vibration can be seen at 2240 cm^{-1} . The peak height ratio between the C=C stretch and the C \equiv N stretch relative to the
30 blank was used for determining the degree of hydrogenation, it being assumed that the stretch

vibration of the nitrile group does not change significantly as a result of the unsaturated polymer being hydrogenated.

5 Example 1

 A solution of 0.68g of H_3BO_3 (11 mmol) and 6.31 g of $N_2H_4 \cdot 1H_2O$ (hydrazine monohydrate, 126 mmol) in 5.5g of water were added to a 250-ml glass three-neck flask equipped with a glass top stirrer, cooler and peristaltic pump and containing 25g of latex, Nysin® 33/3 (a copolymer of 67% butadiene with 33% acrylonitrile) with a polymer content of 25% and containing a total of 77.5 mmol of carbon-carbon double bonds. A few drops of silicone oil were added as defoamer.

 The latex was heated to 40°C and stirred for some minutes. While the contents were being stirred, 13.30 g of a 30% solution of H_2O_2 in water (117 mmol) were added drop-wise during a period of 6 hours with the aid of the peristaltic pump. On being hydrogenated, the 5 grams of latex were poured into 50 grams of isopropanol. The polymer dissolved completely in chloroform (no gel particles were visible). The degree of hydrogenation, determined by 1H -NMR, was 96%.

25

Example 2

 Example I was repeated except that the amount of hydrazine was varied as shown in Table 1. The H_2O_2 was added drop-wise in an equimolar amount relative to hydrazine.

30

All samples dissolved completely in chloroform (no gel

particles were visible).

Ex.	Hydrazine monohydrate (grams)	$\text{H}_2\text{N}-\text{NH}_2 \cdot \text{H}_2\text{O}$ equivalents relative to $\text{C}=\text{C}$	Degree of hydrogenation (%)
II.1	3.1	0.8	70
II.2	3.9	1.0	85
II.3	4.3	1.1	89
II.4	4.7	1.2	93
I	6.31	1.6	96

Table 1. Degree of hydrogenation as a function of the amount of hydrazine.

Example III

Example I was repeated except that the H_2O_2 was added in 12 hours, with two different amounts of hydrazine. Slow addition of hydrogenperoxide gives an increase in the degree of hydrogenation. All samples dissolved completely in chloroform (no gel particles visible).

Ex.	Hydrazine monohydrate (grams)	$\text{H}_2\text{N}-\text{NH}_2 \cdot \text{H}_2\text{O}$ equivalents relative to $\text{C}=\text{C}$	time (hours)	Degree of hydrogenation (%)
III.1	3.9	1.0	12	87
III.2	4.7	1.2	12	97

Table 2. Degree of hydrogenation at 12 hours of reaction time and variable amount of hydrazine.

Example IV

- 5 Example I was repeated except that 4.68 grams of $N_2H_4 \cdot 1H_2O$ (hydrazine monohydrate) and 0.16 grams of boric acid were added, and the reaction was carried out at different temperatures. Low amounts of hydrazine monohydrate and boric acid give a lower
- 10 degree of hydrogenation. The degree of hydrogenation is increased by raising the temperature of the reaction. All samples dissolved in chloroform.

Ex	Temperature (°C)	Degree of hydrogenation (%)
IV.1	40	60
IV.2	70	90

- 15 Table 3. Degree of hydrogenation as a function of temperature

Example V

- 20 Example I was repeated except that the amount of boric acid was varied. Increase of the amount of boric acid, gives an increase in the degree of hydrogenation. All samples dissolved completely in chloroform (no gel particles visible).

Ex.	Boric acid (grams)	Degree of hydrogenation (%)
V.1	0	60
V.2	0.17	80
V.3	0.34	85
V.4	0.51	96
V.5	0.85	93

Table 4. Degree of hydrogenation as a function amount of boric acid added.

5

Example VI

Example IV.1 was repeated, except that boric acid was dissolved in the hydrogenperoxide solution, and added to the latex together with the hydrogenperoxide.

10

The degree of hydrogenation increased considerably upon premixing of boric acid with the hydrogenperoxide.

Ex	Boric acid premixed with H_2O_2	Degree of hydrogenation (%)
IV.1	no	60
VI.1	yes	91

15 Table 5. Effect of premixing of boric acid with hydrogenperoxide.

Example VII

Example IV.1 was repeated, except that ligands L were added to the latex with the boric acid. Addition of ligands increases the catalytic activity of boric acid.

Ex.	Ligand L	gram	Degree of hydrogenation (%)
IV.1	no	--	60
VII.1	ethanol	0.12	70
VII.2	1-phenyl-1,2-ethanediol	0.34	70
VII.3	polyethyleneglycol, OH-terminated, Mw 35.000	0.15	83
VII.4	polyvinylalcohol, 98% hydrolysed, Mw 20.000	0.15	93

Table 6. Addition of ligands L to the reaction mixture.

Comparative experiment A

An amount of $N_2H_4 \cdot 1H_2O$ (hydrazine monohydrate), as shown in Table 1, dissolved in 5.5 grams of water, were added to a 250-ml glass three-neck flask equipped with a glass top stirrer, cooler and peristaltic pump and charged with 25g of latex, Nysin 33/3 with a polymer content of 25%. A few drops of silicone oil were added as defoamer.

-The hydrogenation reaction was carried out as in

Example I, with H_2O_2 in a 30% solution of H_2O_2 in water being added drop-wise with the aid of the peristaltic

pump in an equimolar amount relative to hydrazine.

All samples dissolved completely in chloroform (no gel particles were visible).

Comp. ex.	Hydrazine monohydrate (grams)	$\text{H}_2\text{N}-\text{NH}_2 \cdot \text{H}_2\text{O}$ equivalents relative to $\text{C}=\text{C}$	Degree of hydrogenation (%)
A.1	3.9	1.0	55
A.2	5.9	1.5	67
A.3	7.6	2.0	80
A.4	9.8	2.5	94

5

Table 7. Degree of hydrogenation as a function of the amount of hydrazine required in the absence of boric acid

10 Comparative experiment B

4.3 g of $\text{N}_2\text{H}_4 \cdot 1\text{H}_2\text{O}$ (hydrazine monohydrate, 1.1 equivalent relative to $\text{C}=\text{C}$), followed by 0.0018 grams of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 5 grams of water were added to a 250-ml glass three-neck flask equipped with a glass top stirrer, cooler and peristaltic pump and charged with 25g of latex, Nysin 33/3 with a polymer content of 25%. A few drops of silicone oil were added as defoamer. The latex was heated to 40 °C and stirred for some minutes. While the contents were being stirred, 10 g of a 30% solution of H_2O_2 in water were added drop-wise with the aid of the peristaltic pump. During the hydrogenation, 1-gram latex samples were taken and

20

these were precipitated in 10 grams of isopropanol. The polymer's solubility was directly measured visually in chloroform.

Ex.	H ₂ O ₂ added (%)	Degree of hydrogenation (%) ^{x2}	Solubility
B.1	13.9	14	soluble
B.2	33	28	soluble
B.3	47	-	gelled
A.4	100	71	gelled

5

Table 8. Solubility as a function of H₂O₂ added and degree of hydrogenation

The polymers in Experiments B.3 and B.4 were subjected to a Soxhlet extraction with chloroform, with the aid of which the gel content was determined. The sample in Experiment B.3 contained 70% gel and the sample in Experiment B.4 contained more than 90%. The degree of hydrogenation in Experiment B.4 was determined by Raman spectrometry.

15

Comparative example C

5.8 g of N₂H₄·1H₂O (hydrazine monohydrate, 1.5 equivalent relative to C=C), followed by an amount of CuSO₄·5H₂O as indicated in Table 7 in 5 gram of water were added to 250-ml glass three-neck flask equipped with a glass top stirrer, cooler and peristaltic pump and charged with 25g of latex, Nysin 33/3 with a polymer content of 25%.

20

The latex was heated to 50 °C and stirred for some minutes. While the contents were being stirred, 13.1 g of a 30% solution of H₂O₂ in water were added drop-wise with the aid of the peristaltic pump. After the

5 hydrogenation, 1-gram latex samples were taken and these were precipitated in 10 grams of isopropanol. The polymer's solubility was directly measured visually in chloroform (see Table 7).

10

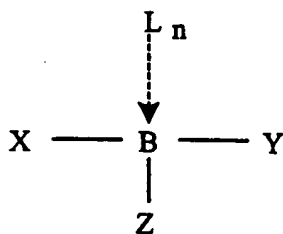
Comp. ex.	CuSO ₄ .5H ₂ O (grams)	Degree of hydrogenation (%) ^{x1}	Solubility
C.1	0.0009	80	gelled
C.2	0.0019	89	gelled
C.3	0.0095	55	gelled
C.4	0.017	32	gelled

Table 9. Solubility as a function of degree of hydrogenation

15 The polymer obtained in each experiment was subjected to a Soxhlet extraction with chloroform. The gel content was found to be higher than 60% in all cases. The degree of hydrogenation of the samples in Comparative Example C was determined by Raman
20 spectrometry.

CLAIMS

1. Process for hydrogenating carbon-carbon double
 5 bonds of an unsaturated polymer by adding to the unsaturated polymer (1) a reducing agent selected from the group comprising hydrazines and hydrazine-releasing compounds, (2) an oxidising compound and (3) a catalyst, characterised in
 10 that the catalyst contains an element from group 13 of the Periodic Table of the Elements.
2. Process according to Claim 1, characterised in that the catalyst is a compound which contains boron.
- 15 3. Process according to Claim 2, characterised in that the catalyst is a compound of the general formula



20

wherein X, Y and Z are chosen independently of one another from the group comprising R, =O, OR, OOR, NR₂, SR, PR₂, OC(=O)R and halogen atoms, where R is a H atom or an alkyl, aryl or
 25 cycloalkyl group having 1-20 carbon atoms, or a hydrocarbon group having 1-20 C atoms and containing a heteroatom from groups 14, 15, 16

and 17 of the Periodic Table of the Elements, or a polymerchain containing one or more polar groups; wherein X and Z and optionally Y may form a bridge;

5 L is an electron-donating ligand, which may be bonded to either X, Y or Z;

n = 0, 1 or 2.

4. Process according to Claim 3, characterised in that the catalyst is boric acid.

10 5. Process according to Claim 4, characterised in that boric acid is used in combination with a polyvinylalcohol.

6. Process according to anyone of claims 1-5, characterized in that the molar ratio of the catalyst to the carbon-carbon double bonds of the
15 unsaturated polymer is between 1:50 and 1:2.

7. Process according to anyone of claims 1-6, characterized in that the oxidising compound is selected from the group consisting of peroxides and hydroperoxides.
20

8. Process according to anyone of Claims 4-7, characterised in that the boric acid is added to the reaction mixture together with the peroxide or hydroperoxide.

25 9. Process according to Claim 7, characterised in that the oxidising agent is hydrogen peroxide.

10. Process according to anyone of Claims 1-9, characterised in that the molar ratio of oxidising compound to carbon-carbon double bonds
30 is between 0.9:1 and 2:1.

11. Process according to any one of Claims 1-10,

characterised in that the molar ratio of hydrazine or hydrazine releasing compound to carbon-carbon double bonds is between 0.9:1 and 2:1.

- 5 12. Process according to any one of Claims 1-11, characterised in that the reducing agent is selected from the group consisting of hydrazine and hydrazine hydrates.
- 10 13. Process according to any one of Claims 1-12, characterised in that the unsaturated polymer is present in the latex form.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/NL 99/00507

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F8/04 C08C19/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F C08C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 452 950 A (L. G. WIDEMAN) 5 June 1984 (1984-06-05) cited in the application column 3, line 27 -column 4, line 9; claims 1-15	1-13
Y	EP 0 801 079 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 15 October 1997 (1997-10-15) page 3, line 52 -page 4, line 26; claims 1-14	1-13
Y	DE 35 20 103 A (BASF AG) 11 December 1986 (1986-12-11) page 3, line 32 -page 4, line 28; claims 1,2; examples 1-4	1-13
	-/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

23 November 1999

Date of mailing of the international search report

01/12/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Permentier, W

INTERNATIONAL SEARCH REPORT

International Application No

PLI/NL 99/00507

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 314 967 A (W. L. HERGENROTHER) 24 May 1994 (1994-05-24) claims 1-10 ---	1-13
A	T. YOSOMIYA: "METALLIZATION OF POLYACRYLONITRILE BY REDUCTION OF POLYMER-INCORPORATED METAL IONS." ANGEWANDTE MAKROMOLEKULARE CHEMIE: APPLIED MACROMOLECULAR CHEMISTRY AND PHYSICS, vol. 197, no. 3400, May 1992 (1992-05), pages 49-58, XP000274695 BASEL, CH page 49 -page 58 ---	1
A	US 4 221 872 A (J. LYDIATE) 9 September 1980 (1980-09-09) column 2, line 57 -column 3, line 2; claims 1-18 ---	1
A	D. K. PARKER: "A NEW PROCESS FOR THE PREPARATION OF HIGHLY SATURATED NITRILE RUBBER IN LATEX FORM." RUBBER CHEMISTRY AND TECHNOLOGY, vol. 65, no. 1, March 1992 (1992-03), pages 245-258, XP000271010 OHIO, US page 245 -page 258 ---	1
A	WO 91 06579 A (OLIN CORPORATION) 16 May 1991 (1991-05-16) cited in the application page 3, line 22 -page 5, line 9; claims 1-7 ---	1
A	PATENT ABSTRACTS OF JAPAN vol. 005, no. 106 (C-062), 10 July 1981 (1981-07-10) & JP 56 045907 A (NIPPON PEROXIDE CO., LTD.), 25 April 1981 (1981-04-25) abstract -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 99/00507

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4452950	A	05-06-1984	AU 559579 B	12-03-1987
			AU 2477584 A	30-08-1984
			BR 8400562 A	25-09-1984
			CA 1216598 A	13-01-1987
			EP 0117221 A	29-08-1984
			ES 529890 A	01-07-1985
			JP 1761774 C	28-05-1993
			JP 4041161 B	07-07-1992
			JP 59161415 A	12-09-1984
			MY 100004 A	26-10-1988
EP 801079	A	15-10-1997	DE 69700309 D	12-08-1999
			ES 2134050 T	16-09-1999
			JP 10036421 A	10-02-1998
			US 5814709 A	29-09-1998
DE 3520103	A	11-12-1986	NONE	
US 5314967	A	24-05-1994	US 5367034 A	22-11-1994
US 4221872	A	09-09-1980	AU 523753 B	12-08-1982
			AU 4141978 A	07-06-1979
			JP 54083092 A	02-07-1979
WO 9106579	A	16-05-1991	US 5057601 A	15-10-1991
			AU 641446 B	23-09-1993
			AU 6645590 A	31-05-1991
			CA 2073004 A	07-05-1991
			DE 69021580 D	14-09-1995
			DE 69021580 T	18-04-1996
			EP 0500650 A	02-09-1992
			ES 2077080 T	16-11-1995
			JP 6039489 B	25-05-1994
			JP 5504782 T	22-07-1993
JP 56045907	A	25-04-1981	JP 1334117 C	28-08-1986
			JP 60056164 B	09-12-1985